

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### A Method of Processing Waste of Polyethylene Terephthalate by Hydrolysis

We, JAROSLAV PITAT, of No. 179, Brankovice, CYRIL HOLCIK, of No. 1551, VARSAVSKA, Gottwaldov, and MILOS BACAK, No. 3865, Leninova, Gottwaldov, all of Czechoslovakia, and all citizens of Czechoslovakia, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of processing waste of polyesters, particularly of polyethylene glycol terephthalate, by hydrolysis.

15 It is known that organic esters may be split by strong acids or bases. Polyesters exhibit, however, a different behaviour in this respect and their splitting is more difficult. It has been proposed already to split 20 polyethylene terephthalate waste into terephthalic acid and glycol by treating material resulting from the granulation of polyethylene terephthalate in the form of little pieces, waste of filaments, yarn, textiles and nets, in 25 certain cases mixed with other natural or artificial fibres. For this purpose the waste was heated under reflux with strong mineral acids or glycols. As mineral acids concentrated sulphuric or hydrochloric acid and as 30 glycol preferably ethylene glycol has been used. (See British Specification number 762,690). The reaction temperature has been maintained within the range of the boiling point of these agents. The literature does 35 not mention the results obtained by these splitting methods. A disadvantage of these methods consisted evidently in the necessity of using the mentioned agents in excess, thus raising the costs of the treatment, particularly 40 when using ethylene glycol.

According to the present invention it has been discovered that practically a complete hydrolysis of the polyethylene terephthalate can be achieved by the action of aqueous 45 alkali metal hydroxide solution, e.g. sodium

hydroxide solution, and that by an appropriate adjustment of the concentration of the alkali metal solution a maximum salting out effect for the alkali terephthalate formed in the reaction solution can be attained. The 50 hydrolysis of polyethylene terephthalate is preferably carried out at a temperature of about 100°C and takes two hours. The salting out of the alkali metal terephthalate during the alkaline hydrolysis decreases the 55 consumption of the alkali metal hydroxide nearly up to the theoretical amount, because the hydroxide excess necessary for the adequate speed of the hydrolysis and present in the filtrate may be utilized in further 60 hydrolyses after the separation of the well filterable alkali metal terephthalate precipitate and after resaturation of the filtrate up to the initial concentration. During the hydrolysis ethylene glycol is formed. By 65 repeated utilization of the alkali metal terephthalate filtrate it is concentrated in the solution and can be then advantageously recovered by vacuum distillation.

The action of the aqueous alkali metal 70 solutions upon the polyethylene terephthalate is very effective. During the hydrolysis the alkali metal salt of terephthalic acid, which is rather soluble in aqueous alkali metal solutions, is separated. This salt is dis- 75 solved in a small quantity of water to obtain a nearly saturated solution and by acidifying this solution terephthalate acid is precipitated, filtered off washed and dried. By a suitable adjustment of the sodium 80 hydroxide concentration to 18 per cent a nearly complete salting out of sodium terephthalate from the reaction mixture can be attained. Nevertheless a portion of the terephthalate remains in the form of a 0.5 85 per cent solution. The proportion by weight of polyethylene terephthalate to the alkali metal hydroxide solution may be from 1 to 20.

The solubility coefficient of the alkali 90

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metal terephthalate can be decreased in accordance with a further feature of the invention by carrying out the hydrolysis in an aqueous alcoholic medium, preferably having a water-alcohol ratio of 1:1. In this way higher yields of terephthalic acid can be achieved due to more limited losses in the filtrate and due to the quicker progress of the reaction at lower temperature. The process can be carried out at a much lower concentration of the base in the hydrolytic solution. The reaction can proceed under normal as well as under increased pressure, the latter case enabling lowering the alkali metal content to a minimum. The hydrolysis of the polyethylene terephthalate can be carried out under pressures up to 250 atmospheres. When performing the hydrolysis of the polyethylene terephthalate in an alcoholic solution under pressure in the presence of small quantities of alkali metal only, i.e. 0.7 to 2.0 per cent sodium hydroxide referred to the polyethylene terephthalate, esterification of the terephthalic acid by the respective alcohol takes place at the same time, the ester precipitating in crystalline well filterable form.

#### EXAMPLE 1

1 part by weight of polyethylene terephthalate waste is heated with 20 parts by weight of an 18 per cent aqueous sodium hydroxide solution at a temperature of 100°C under reflux for 2 hours. The major proportion of the sodium terephthalate separates in the form of a well filterable grayish-white precipitate. This precipitate is filtered off and on the filter dissolved in such an amount of hot water to obtain a nearly saturated approximately 13 to 14 per cent sodium terephthalate solution.

The sodium terephthalate solution is heated up to 70° to 80° and acidified with sulphuric acid, whereby terephthalic acid is precipitated. The acid is filtered off, dried and then converted into dimethyl-terephthalate. The filtrate, after removing the separated sodium terephthalate precipitate but containing still about 0.5 per cent of this salt, is resaturated with solid sodium hydroxide to obtain again an 18 per cent sodium hydroxide solution which is utilized in further hydrolyses of polyethylene terephthalate.

The yield of terephthalic acid in the first hydrolysis amounts to up to 94 per cent of the theory, approximately 6 per cent of the terephthalic acid remaining in the solution in the form of its sodium salt. When using the reaction mixture resaturated with sodium hydroxide repeatedly, nearly theoretical yields of terephthalic acid can be obtained and at the same time freed glycol can be accumulated in the filtrate for further economical recovery.

1 kg of terephthalic acid consumes in this

process 0.8 kg of solid sodium hydroxide. The process described is not only economical, but also unobjectionable with regard to the purity of waste waters which are not contaminated by glycol containing spent lyes.

#### EXAMPLE 2

One part of polyethylene terephthalate, 2 parts of solid potassium hydroxide and 16 parts of 99.7 per cent methanol are heated in a container with stirrer and reflux on a water bath for 1 hour. The precipitated potassium terephthalate is filtered off, and while on the filter it is dissolved in a minimum amount of water; by acidification of the solution terephthalic acid is precipitated, and it is filtered off, washed and dried. The alcoholic filtrate obtained before is resaturated with potassium hydroxide and used again in further hydrolyses.

The yield amounts to 0.84 parts of terephthalic acid, equal to 98 per cent of the theoretical amount.

#### EXAMPLE 3

The process according to Example 2 is followed up with the difference that instead of methanol the same amount of 97.8 per cent ethanol is used.

The yield amounts to 0.83 parts of terephthalic acid, equal to 96 per cent of the theory 95 approximately.

#### EXAMPLE 4

The process according to Example 2 is pursued with the difference that instead of pure methanol 18 parts of 50 per cent methanol are used.

The yield amounts to 0.81 parts of terephthalic acid equal to about 95 per cent of the theoretical amount.

#### EXAMPLE 5

To 1 part of fibrous polyethylene terephthalate waste 8.6 parts of 99.7 per cent methanol and 0.01 parts of sodium hydroxide are added and the mixture is heated in a pressure vessel with stirrer at a temperature of 144°C. and a pressure of 12 atmospheres for 3 hours. After cooling a crystalline mixture was obtained containing 0.5 parts of dimethylterephthalate and 0.4 parts of monomethylterephthalate which was filtered off. The mother liquor which can be re-used in further hydrolyses contained after filtration beside methanol about 0.86 per cent of dissolved dimethylterephthalate and liberated glycol.

#### EXAMPLE 6

400 parts of polyethylene terephthalate waste filaments, 3200 parts of commercial 99.1 per cent methanol and 3 parts of potassium hydroxide are heated in an autoclave in an inert atmosphere of nitrogen at a temperature of 232°C. and a pressure of 50 atmospheres for 1 hour. After cooling 340.1 parts of crystals were filtered off containing 85 per cent dimethylterephthalate and 13

per cent monomethylterephthalate. A small amount of dimethylterephthalate remained dissolved in the methanol. The mother liquor can be used directly in another hydrolysis under pressure. Finally dimethylterephthalate and glycol may be recovered from the mother liquor by distillation.

The process according to the invention enables processing economically waste of polyethylene terephthalate even mixed with other substances, into valuable raw materials.

#### WHAT WE CLAIM IS:—

1. A method of processing waste of polyethylene terephthalate by hydrolysis, in which the hydrolysis is carried out by heating with an alkali metal hydroxide solution, the liberated terephthalic acid, salted out from the solution in the form of an alkali metal terephthalate is filtered off, washed and subjected to further treatment.
2. A method as claimed in Claim 1, wherein the proportion by weight of polyethylene terephthalate to the alkali metal hydroxide solution, preferably 18 per cent sodium hydroxide solution, is 1 to 20.
3. A method as claimed in Claims 1 or 2, wherein the hydrolysis is carried out under pressure which may be increased up to 250 atmospheres.
4. A method as claimed in Claim 1, wherein the separated alkali metal terephthalate is dissolved in a small quantity of water to obtain a nearly saturated solution and by acidifying this solution terephthalic acid is precipitated, filtered off, washed and dried.
5. A method as claimed in Claim 1,

wherein the filtrate after the separation of the precipitated alkali terephthalate is repeatedly used in the hydrolysis by resaturating it with solid alkali metal hydroxide to the required concentration.

6. A method as claimed in Claim 1, wherein the hydrolysis is carried out by means of an alcoholic, preferably a methanolic or ethanolic, alkali metal hydroxide solution.

7. A method as claimed in Claim 1, wherein the hydrolysis is carried out by means of an aqueous alcoholic alkali metal hydroxide solution, preferably in a ratio of water to alcohol equal to 1:1.

8. A modification of the method as claimed in Claim 1, wherein the hydrolysis is carried out in a medium of a methanolic solution in the presence of 0.7 to 2.0 per cent alkali metal hydroxide referred to the polyester, under pressure to obtain in a single stage a crystalline and filterable mixture of a monomethylterephthalate and dimethylterephthalate.

9. A method of processing waste of polyethylene terephthalate by hydrolysis, substantially as described in the specification with reference to any of the examples.

10. Terephthalic acid, its esters and alkali metal salts, when regenerated by a method claimed in any of Claims 1-7 and 9.

11. Methyl esters of terephthalic acid when recovered by a method according to Claim 8.

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